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PBI Reverse Osmosis Membrane for Chromium Plating Rinse Water

American Electroplaters' Society, Inc, Winter Park, Fla

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16. ABSTRACT

A laboratory research study was carried out to select and optimize polybenzimidazole(PBI) reverse osmosis(RO) membranes for the treatment of chromium plating rinse water. The effects of important film casting and annealing variables on RO properties were investigated. Membranes were tested in high pressure flow cells with dilute sodium chloride and chromic acid feed solutions.

PBI RO membranes were found to be resistant to attack by chromic acid. After pretesting with sodium chloride, the membranes showed a short-term effective level of rejection with chromic acid. Upon retesting with sodium chloride, the same membranes again exhibited high salt rejections, thereby demonstrating they had not been chemically attacked by chromic acid.

A significant improvement in long-term rejection of chromic acid was obtained when the membranes were pretreated with sodium tungstate solution. The addition of sodium tungstate to the feed solution further improved chromic acid rejection. Highest levels of chromic acid rejection were obtained by adjusting the pH of the feed. However, neither pH adjustment nor addition of tungstate to the feed are acceptable in practice because of possible contamination of the plating bath by the extraneous ions. The project failed to develop an acceptable PBI RO membrane for treating chromium plating rinse water.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. It was a laboratory scale research study to assess the potential utility of recently developed polybenzimidazole membranes in a reverse osmosis system for the treatment of chromium plating rinse waters. Feasibility studies had demonstrated that PBI possessed the requisite chemical stability to withstand long-term contact with chromic acid waste streams where other, earlier membranes, such as cellulose acetate and polyamides, have failed. The results of the report are of value to R & D programs concerned with the treatment of wastewaters from various metal finishing, nonferrous metal, steel, inorganic and other industries. Further information concerning the subject can be obtained by contacting the Metals and Inorganic Chemicals Branch of the Industrial Pollution Control Division.

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ABSTRACT

The objective of this laboratory research study was to develop a high temperature, oxidation-resistant reverse osmosis (RO) membrane for the treatment of metal finishing effluents. Specifically, the study was directed to the selection and optimization of a flat polybenzimidazole (PBI) membrane to treat chromium plating rinse water.

Important variables in casting PBI films and subsequent heat treatment were investigated to assess their effects on membrane RO properties in this application. Membranes were tested on a high pressure circulating flow system in flat film test cells. Membrane screening tests were carried out by pretesting them with sodium chloride feed solution at 5,000 ppm concentration. Membranes with optimum properties were then tested with a simulated rinse water containing 200 ppm chromic acid or with authentic plating bath solution diluted to 200 ppm chromic acid.

PBI RO membranes were found to be resistant to attack by chromic acid. After pretesting with dilute sodium chloride solution, the membranes showed a short-term effective level of rejection with chromic acid. Upon retesting with sodium chloride, the same membranes exhibited high salt rejections, thereby demonstrating that they had not been chemically attacked by chromic acid.

A significant improvement in long-term rejection of chromic acid was obtained when the membranes were pretreated with 5,000 ppm sodium tungstate solution. The continuous addition of sodium tungstate to the feed solution further improved chromic acid rejection. However, this approach to long-term high level rejection of chromic acid is not acceptable in practice because of the possible contamination of the plating bath by tungstate ions.

Another approach to long-term high level chromic acid rejection involves pH adjustment. In this case, no pretreatment or preconditioning of the membrane is required. When the pH of the feed was raised from 2.9 to 4.0 with sodium hydroxide, an 80% chromic acid rejection resulted. Adjustment of the pH to 5.7 with ammonium hydroxide increased the chromium rejection level to 95%. Again, this approach turned out to be unacceptable in practice because of the possible introduction of extraneous ions into the working bath. The project failed to develop an acceptable PBI RO membrane for treating chromium plating rinse water.

This report was submitted in fulfillment of Grant No. R-803620 by the American Electroplaters' Society under the sponsorship of the U.S. Environmental Protection Agency. The report covers work performed in the period between March 15, 1975 and December 15, 1976.

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I. INTRODUCTION

GENERAL

Electroplating and metal finishing waste streams are significant contributors to stream pollution. This occurs either directly, owing to the content in the effluents of such toxic and corrosive materials as cyanides, acids and metals, or indirectly, as a result of the deleterious effects these compounds exert on sewage treatment systems. Effective waste treatment methods are needed by the metal processing industries to meet the stringent effluent guidelines for 1977 and the more stringent guidelines proposed for 1983 and 1985. Satisfactory methods exist for the removal and recovery, if warranted, of most metals from plating waste waters, but chromium remains a problem.

Chromium can be removed from waste or rinse water by a number of methods -- chemical treatment, evaporation or ion exchange. Chemical treatments methods are commonly practiced. These include the reduction of hexavalent chromium to trivalent chromium by reagents such as sulfur dioxide, sodium bisulfite or ferrous sulfate, followed by neutralization to precipitate the metal; precipitation of hexavalent chromium by barium chloride or sodium hydroxide; neutralization by sodium hydroxide, limestone, sodium carbonate, etc. Chemical treatment methods, however, pose the vexing problem of sludge and liquid waste disposal. Moreover, there is an economic loss of valuable chromium. It would be preferable to recover and recycle the chromium as well as the purified water.

PRINCIPLES OF REVERSE OSMOSIS

Reverse osmosis, a relatively new membrane process discovered about 17 years ago and originally aimed at providing potable water from brackish water, has aroused great interest in major industries, such as food, textiles, chemical, metal processing, etc. It involves the pressure-activated transport of water through a semipermeable membrane by a selective solubility process in which water dissolves and is subsequently transmitted to an extent much greater than that for dissolved solutes. Pressure, in excess of the solution's osmotic pressure, acts preferentially to enhance the selective permeation of water; solute-flux is essentially pressure-insensitive.

The equations describing the transport of water and solute through a membrane are:

$$J_1 = A(\Delta P - \Delta \pi)$$
$$J_2 = D_2 K \frac{\Delta C}{\Delta X}$$

where J_1 and J_2 are water and solute fluxes. ΔP is the pressure difference across the membrane; $\Delta \pi$ is osmotic pressure difference and A is a membrane constant related to the diffusion coefficient and solubility of water in the membrane. D_2 is the solute diffusion coefficient; K is the distribution coefficient for the solute between membrane and solution; ΔC is the concentration difference on the two sides of the membrane; and ΔX is the effective membrane thickness.

APPLICATION OF REVERSE OSMOSIS TO METAL FINISHING WASTE TREATMENT

Reverse osmosis offers the potential for achieving closed loop control for treating metal finishing waste waters. Previous studies have shown that RO is both technically and economically feasible for some plating waste streams. Particular advantages of RO over other recovery processes include:

Low capital cost. The modular nature of RO units make them particularly well-suited for small-scale installations.

Low energy cost. Only power for pumping is required.

Low labor cost. The process is simple to operate since it involves primarily the pumping of liquids.

Low space requirements. RO equipment is compact and operates continuously, requiring minimal tankage.

No sludge. There are only two exit streams: purified water return to the rinse bath, and concentrated metal solution return to the finishing bath.

On the basis of pilot plant investigations sponsored by the Environmental Protection Agency and the American Electroplaters' Society, reverse osmosis appears to be attractive for treating rinse waters from Watts nickel, nickel sulfate (acid copper), copper pyrophosphate, zinc chloride, and copper-zinc and cadmium cyanide baths, as well as total plant effluents. However, the technique has not yet been found workable for chromium wastes which need more chemically stable membranes.

PBI REVERSE OSMOSIS MEMBRANES

The potential of the polybenzimidazole (PBI) polymer, poly-2, 2'-(m-phenylene)-5, 5'-bibenzimidazole, prepared as described by Conciatori et al[1], as a reverse osmosis membrane was explored several years ago. RO properties of flat PBI membranes were found to be comparable to cellulose acetate at ambient conditions and significantly superior at elevated temperature. The polymer is known to possess outstanding thermal, physical and chemical stability over a wide pH range and a high affinity for water. Its solubility in N, N'-dimethylacetamide (DMAc) permits easy conversion of polymer to fiber or flat film.

In a series of research studies concerned with morphological and transport characteristics, PBI membranes were found to possess useful, long-term RO properties in both hollow fiber and flat film configurations (2, 3, 4, 5). PBI's oxidative resistance to, and stability in, high levels of chlorination in the seawater desalination study [3] and its resistance to strong acid made it an attractive RO candidate for chromium plating rinse water application where earlier membranes, including cellulose acetate and polyamides, cannot be used.

In this research project, PBI RO membranes were evaluated in flat film configuration with a simulated rinse water containing 200 ppm chromic acid. Major efforts were devoted to the optimization of membrane properties as influenced by fabrication variables and post treatment techniques, including those based on reacting the basic -NH- groups of polybenzimidazole with reactive agents to favorably alter transport properties.

II. CONCLUSIONS

Pretreatment of PBI RO membranes with sodium tungstate significantly improves the long-term rejection of chromic acid over that of the untreated membrane. Newly fabricated, untreated membranes exhibit low chromic acid rejection levels. The tungstate treatment markedly increases the rejection which remains effective for at least nine days. Even higher rejection levels are achieved when 100 ppm sodium tungstate is added to the chromic acid feed solution. However, the addition of extraneous ions, such as tungstate, to chromium plating rinse water would not be acceptable in practice since it would not be feasible to recycle the chromium solution containing tungstate ions.

Other conditioning or treatment agents tested were not as effective as sodium tungstate. With sodium chloride, only a short-term beneficial effect is observed.

Optimum RO membrane properties are obtained from PBI films cast from a dimethylacetamide solution containing 18% polymer by weight, coagulated in water at room temperature, and annealed in ethylene glycol for 10 minutes at 165°.

PBI RO membranes are resistant to attack by chromic acid. The intrinsic RO properties are not affected by several weeks exposure to 200 ppm chromic acid feed solution at pH 2.9-3.0. This is demonstrated by the high salt rejection achieved after testing with chromic acid solution.

Adjustment of the feed pH by addition of sodium hydroxide or aqueous ammonia yields the highest chromic acid rejection levels and an increase in water flux, without pretreatment or preconditioning of the membrane. Rejection levels as high as 95% were obtained on adjusting feed pH from pH 2.9 to pH 5.7 with aqueous ammonia. As with the tungstate addition to the rinse water, pH adjustment is not acceptable in practice because of the possible buildup of harmful salts in the plating solutions.

Although membrane performance was improved by feed pH adjustment and membrane treatment, the project failed to develop a PBI membrane which would be acceptable or satisfactory for the treatment of chromium plating rinse water.

III. RECOMMENDATIONS

In view of the demonstrated improved level of chromic acid rejection obtained with PBI RO membranes by pretreatment with sodium tungstate and the demonstrated polymer's resistance to chromic acid, it is recommended that the study be continued on a laboratory scale to develop a membrane with higher long-term rejection levels without the addition of agents to the feed solution.

IV. EXPERIMENTAL

MEMBRANE CHARACTERIZATION

A high pressure, closed loop, circulating flow loop with flat film test cells taking 2 - inch membrane circles was assembled. The system was described in an earlier study [5] and is shown in Figure 1. Feed solution from a five-gallon feed tank was pumped through the test cells by a positive displacement Lapp diaphragm pump rated for 1500 psi service at a flow rate of about 20 gallons per hour. From the pump, the feed passed to the manifold on which 12 cells were mounted in series. The membrane sample, 1.9 inches in diameter, was placed in the cell on top of a filter paper circle and supported underneath by a porous steel disc. Cell diameter was 1.9 inches and the chamber clearance of 0.090 inches over the membrane sample resulted in a linear feed flow rate of about 65 feet/min. Operating pressure was controlled by a back-pressure regulator. Feed composition was maintained constant over an extended test period by returning permeate to the feed tank by means of a small return pump. The chromic acid feed solution was changed about every two days because it reacted with parts of the metal system and slowly changed in concentration. Percent conversion i.e., the ratio of product volume removed to feed volume, was essentially zero since negligible volumes of permeate were removed for analyses.

Flux, percent chromic acid rejection (%R) and pH of feed and product were determined. Flux is the volume rate of flow of permeate per unit membrane area and was determined by timing the volume of permeate flowing into a graduated cylinder. It is expressed as gallons per square foot per day (gfd).

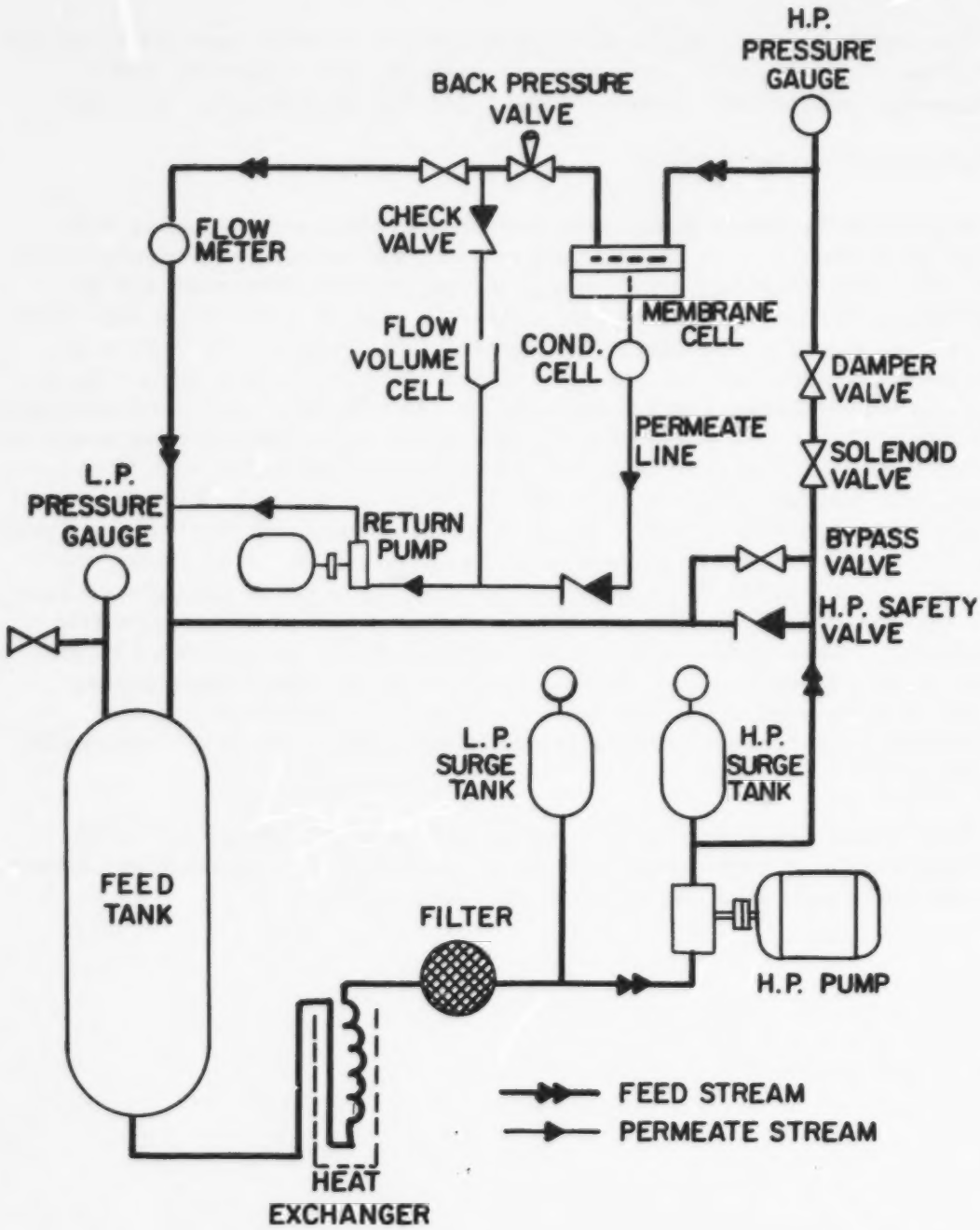
The percent rejection, %R, of solute is defined as:

$$\%R = \frac{C_f - C_p}{C_f} \times 100$$

where C_f = solute concentration in the feed
C_p = solute concentrations in the product

Chromium concentration was determined by a spectrophotometric method [7] based on measuring the absorbance at 540 nanometers of the highly colored chromium-diphenylcarbazide complex. A Beckman recording spectrophotometer, DB-GT, was used. Atomic absorption analyses were also

FIGURE 1 EXPERIMENTAL REVERSE OSMOSIS TEST SYSTEM



carried out on selected samples to verify the accuracy of the spectrophometric method.

Measurements of pH on feed and permeate samples were made with a Beckman SS-2 pH meter.

Concentrations of sodium chloride in sodium chloride feed solutions and permeate samples were obtained by conductivity measurements with a Radiometer conductivity meter, Model CDM 2nd (Copenhagen, Denmark.)

MEMBRANE OPTIMIZATION

Important variables in the film casting operating and annealing step which were studied included (1) polymer concentration in the casting solution, (2) water coagulation bath temperature, (3) film thickness and (4) annealing conditions (time and temperature). The 4" x 12" films were cast on glass plates in a laboratory film casting unit, dried 60 seconds in an air drying chamber and then immersed in water coagulation baths. As a result of the operations an asymmetric film is obtained. Polymer solutions with 16%, 18% and 20% polymer in dimethylacetamide (DMAc) were prepared by diluting a 24% PBI dope to the target solids concentration with DMAc. Coagulation temperatures of 25°C and 5°C were employed. Film thickness ranged from 2 mils to 5 mils. Annealing was carried out in ethylene glycol at 165°C and 180°C and in polyethylene glycol at 220°C. It is during the annealing step that the RO properties are developed in the thin, dense surface (the air side of the film as cast onto glass plate) of the asymmetric membrane. This active layer, about 1 micron thick, is supported by the open, porous substructure. The films were lightly constrained during annealing to prevent distortion but not completly constrained because shrinkage, even though small, was sufficient to cause tears and cracks in the film.

Post treatment of membranes included treating the membrane with inorganic salts or with strong acid to prevent or reduce interaction between the -NH-groups in PBI and chromic acid feed solution.

V. RESULTS AND DISCUSSION

The effects of film casting variables and annealing conditions on RO properties are summarized in Table 1. These data were obtained with a 5,000 ppm sodium chloride feed solution at pH 6.4. Duplicate samples were tested and the values reported are the averages. Membrane casting and annealing conditions for each sample are given. These are, in the order presented: casting solution concentration; film coagulation temperature; annealing medium, (ethylene glycol and polyethylene glycol); annealing temperature; and wet film thickness.

These results indicate that the best combination of RO properties was obtained with films cast from 18% solutions (dopes) and annealed in ethylene glycol at 165°C. An annealing time of 10 minutes was adequate. Annealing times as long as 30 minutes are detrimental while annealing times of less than 5 minutes do not develop as good RO properties. Membrane sample F-1, 2 is typical of these preparative conditions. It exhibited good flux, 27.6 gfd, and rejection, 83% after 24 hours (this would improve with time) against 5,000 ppm sodium chloride feed. Flux decreases and rejection improves with time due to pressure-induced compaction and tightening up of the membrane. This effect is noted for samples B, C, G and H. Membranes from the 20% solution exhibited properties equivalent to F-1, 2. Coagulation temperature does not appear to have any effect on RO properties; hence, room temperature is preferred as a matter of convenience.

Membrane thickness of 4-5 mils proved to be adequate to withstand sustained, high pressure operation. Film thickness less than 2.5 mils proved to be inadequate. This is shown for membrane samples D and E, Table 1, both of which failed under pressure testing at 600 psi.

Annealing studies in ethylene glycol showed no real difference in membrane RO properties between 165° and 180° annealing temperatures. The lower annealing temperature was adopted as the standard in membrane fabrication. Membranes annealed at a much higher temperature, e.g. 220°C, in polyethylene glycol, exhibited poor RO properties, as shown by the very low flux values and low rejection levels for membrane sample 1-A in Table 1.

Films were cast at room temperature from 16%, 18% and 20% solutions of PBI in dimethylacetamide to assess the effect of polymer concentration

TABLE 1 EFFECT OF FILM CASTING AND ANNEALING CONDITIONS ON MEMBRANE RO PROPERTIES

Membrane Samples	Casting, Annealing Conditions*	Total Test Hours	Flux gfd	Rejection %
B-1, 2	16%, RT, EG, 165°, 4 mils	24	18.8	84
		192	17.2	89
C-1, 2	16%, 5°C, EG, 165°	24	16.9	64
	4 mils	192	15.2	73
D	18%, RT, EG, 165°,			
	2 1/2 mils	(Too thin; failed)		
E	18%, 5°C, EG, 165°C,			
	2 1/2 mils	(Too thin; failed)		
F-1, 2	18%, RT, EG, 165°C,	24	27.6	83
	4-5 mils			
G-1, 2	18%, RT, EG, 180°C,	24	21.3	86
	4-5 mils	48	19.7	87
H-1, 2	18%, 5°C, EG, 165°C	24	23.0	86
	4-5 mils	48	19.5	88
1-A	18%, RT, PEG, 220°C,	75	0.4	52
	4-5 mils	92	0.3	53
A-1, 2	20%, RT, EG, 165°C,	192	11.4	89
	3 mils			

Test Conditions: 600 psig, 25°C, 20 gal/hr, 0% conversion
Feed Solution: Sodium Chloride, 5,000 ppm, pH 6.4

*EG-Ethylene glycol
PEG-Polyethylene glycol
RT -Room temperature

on film and membrane properties. Casting solutions with 18% polymer concentration were found to yield the best combinations of film strength, solution viscosity, film casting speed, film thickness control and RO properties. This therefore was adopted as the standard solids concentration.

Membrane samples from Table 1 were selected for long-term testing with sodium chloride solution before proceeding to the critical testing with chromic acid feed solution. Membrane samples A and B performed well through 420 hours with sodium chloride. This is shown in Table 2. Rejection levels were 94% and 88% and flux values were 10 gfd and 17 gfd, respectively, for samples A and B. Samples F and H also exhibited good RO properties with the sodium chloride feed solution.

The feed solution was then changed at the 420th hour from dilute sodium chloride to 180-200 ppm chromic acid, as shown in Table 2. Through the next 72 hours, i.e., from 420 to 490 total test hours of testing with chromic acid, all four membrane samples were performing effectively in rejecting chromic acid. The rejection values ranged from 62% to 69% and the flux values ranged from 5 gfd to 12 gfd. Feed pH was 2.9-3.0 and product pH was 3.3-3.4. However, the next 48 hours of testing with chromic acid revealed a rapid deterioration in RO properties. Chromic acid rejection values dropped sharply and after 5 days (120 hours) testing with chromic acid had declined to 10% and less for all four samples. In addition, a decline in water flux was observed over this period. Some of the decline in chromic acid rejection level can be attributed to the lower flux but the total drop in rejection level far exceeds that attributed to flux decline.

Fresh, unconditioned membranes were then tested against chromic acid first, followed by sodium chloride feed solution to determine whether or not the membranes were irreversibly attacked by chromic acid. A preliminary indication that the membranes were not attacked by chromic acid was available from the flux data in Table 2. The fact that the product flux did not increase as the chromic acid rejection dropped sharply, strongly suggested that the membranes were not attacked. Table 3 shows rejection/flux data for fresh membranes, including one (J) which was cross-linked with perfluoroglutaric acid in an attempt to prevent the basic imidazole nitrogens in PBI from reacting with chromic acid. All three membranes exhibited very low rejections of chromic acid. After 72 hours, the rejection values for samples J and L were less than 10%. Surprisingly, Sample K showed a slight increase in rejection during the 72 hours test period. This behavior is typical of RO membranes in which pressure-induced compaction results in a tightening of the membrane and a consequent increase in rejection.

Additional long-term testing was carried out to assess the effects of

TABLE 2. LONG-TERM RO PROPERTIES WITH SODIUM CHLORIDE AND CHROMIC ACID FEED SOLUTIONS

		Membrane Sample							
		A		B		F		H	
Feed	Test Hours	Reject. %	Flux gfd	Reject. %	Flux gfd	Reject. %	Flux gfd	Reject. %	Flux gfd
NaCl	24	93	15.0	84	18.5				
	48	94	14.5	87	17.5				
	145	94	12.5	88	16.0				
	170	95	12.5	88	16.0				
	240	95	12.0	89	15.0				
	392	93	10.5	88	17.0	82	26.5	86	23
	420	94	10.0	88	17.0	83	--	89	19.0
CrO_3	440	62	5.5	66	11.5	69	17.0	69	13.0
		70	5.0	74	10.0	77	14.0	75	11.5
	492	65	5.2	62	11.0	65	12.0	63	10.3
	518	21	5.0	25	9.3	27	10.0	29	8.7
	542	3	4.0	11	7.5	10	9.0	3	10.3

Test Conditions: 600 psig; 25°C; 20 gal/hr; 0% Conversion.

Feed Solutions; NaCl, 5,000 ppm, pH 6.4.
CrO_3, 180-200 ppm, pH 2.8-3.0.

TABLE 3. RO PROPERTIES OF UNCONDITIONED MEMBRANES

Feed	Test Hours	Membrane Sample J Reject. %	J Flux gfd	K Reject. %	K Flux gfd	L Reject. %	L Flux gfd
CrO_3	20	13	10.5	15	2.8	9	13.5
	44	4	6.2	15	2.0	3	6.8
	72	4	5.3	22	1.5	6	4.7
NaCl	92	61	5.5	83	2.0	54	5.0
	116	64	5.0	87	1.8	53	4.5
	140	66	5.5	88	2.0	56	5.0
	230	65	5.0	93	1.8	55	4.5

Test Conditions: 600 psig; 25°C; 20 gal/hr; 0% conversion.

Feed Solutions: NaCl; 5,000 ppm; pH 6.4.
CrO_3; 200 ppm; pH 2.8.

membrane pretreatment, pH adjustment and annealing conditions on RO properties. Test results are given in Table 4.

It is concluded from these test data that neither the chemical nor physical integrity of the PBI membrane is affected by long-term exposure to dilute chromic acid. This is substantiated by the high rejection levels - 80% with chromic acid adjusted to pH 4.0 and 96% with sodium chloride - achieved in subsequent testing with these feed solutions. The beneficial effect of pH adjustment is striking, with rejection of hexavalent chromium increasing from 20% to about 80%. This is presumable due to the formation of sodium dichromate salt upon addition of sodium hydroxide to adjust the pH.

The membranes in Table 4 were cast from 18% polymer solutions, and all, except sample 2A, were annealed in ethylene glycol at 165°C. Sample 2A was annealed in polyethylene glycol at 220°C, which resulted in poor RO properties. Very low flux values, 0.4-0.5 gfd, were obtained. Membranes 1B and 2A were pretreated with 10% sulfuric acid before testing in an attempt to improve the RO properties. No significant effect was noted, however.

Following the feed pH adjustment which sharply increased the rejection of chromium (+6), and changing back to 5,000 ppm sodium chloride feed, the membranes exhibited excellent salt rejection. Rejections of 93% and better were obtained, thereby demonstrating that PBI is resistant to attack by chromic acid. Upon replacing the sodium chloride test feed with 200 ppm chromic acid feed, these membranes again exhibited a sharp drop in chromic acid rejection. The sequential test results in Table 4 are presented in Figure 2 for a convenient overview of RO properties obtained with the different feed solutions and membrane treatments.

The RO properties of PBI membranes were improved when the membranes were pretreated with sodium tungstate. The objective was to form a complex of the anion with the reactive, basic NH groups in the polymer in order to prevent their interaction with chromic acid. However, to be effective, the resultant PBI-tungstate complex must be sufficiently stable and non-leachable when exposed to dilute chromic acid solution. The membrane samples from Table 4, were, therefore, conditioned with sodium tungstate solution by exposing them to a 5,000 ppm sodium tungstate feed solution for 48 hours in the high pressure flow loop. At the end of this period, the membranes were then tested again with chromic acid. The results are presented in Table 5.

A significant improvement in long-term chromic acid rejection was obtained. After 9 days testing against 200 ppm chromic acid feed, the rejections levelled off, ranging from 42% to 55% for three samples. This was

TABLE 4. EFFECT OF SEQUENTIAL FEED CHANGES ON MEMBRANE RO PROPERTIES

		Membrane Sample							
		1		1B*		2A*		3**	
Feed	Hours	Reject. %	Flux gfd	Reject. %	Flux gfd	Reject %	Flux gfd	Reject %	Flux gfd
NaCl	75	90	11.0	86	9.5	83	1.6		
	96	92	10.1	88	8.9	85	1.4		
CrO_3	112	74	2.3	76	2.6	97	0.5		
	132	41	2.0	43	2.4	64	0.4		
	156	19	2.2	19	2.6	30	0.4		
	225	16	2.0	20	2.4	33	0.4		
Adjust	250	57	1.9	58	2.1	52	0.5		
pH to	275	73	1.8	74	1.9	(Removed)			
4.0	300	75	- -	77	- -				
	395	78	1.6	81	1.7			76	- -
	420	78	1.6	81	1.7			76	5.1
	448	81	1.7	84	1.6			78	4.4
NaCl	525	95	3.1	93	2.8			96	9.2
CrO_3	545	68	1.4	69	1.6			70	4.8
	582	36	1.2	37	1.3			37	3.9
	606	14	1.3	18	1.2			14	4.1
	630	22	1.4	20	1.4			19	4.5
	707	24	1.1	25	1.0			22	3.4

*Pretreated with sulfuric acid.
**Same membrane as 1, but without NaCl conditioning.

Test Conditions: 600 psig; 25°C; 20 gal/hr; 0% conversion.
Feed Solutions: NaCl; 5,000 ppm; pH 6.4.
CrO_3; 200 ppm; pH 2.8.

FIGURE 2. RO PROPERTIES OF PBI MEMBRANES IN SEQUENTIAL FEED CHANGES

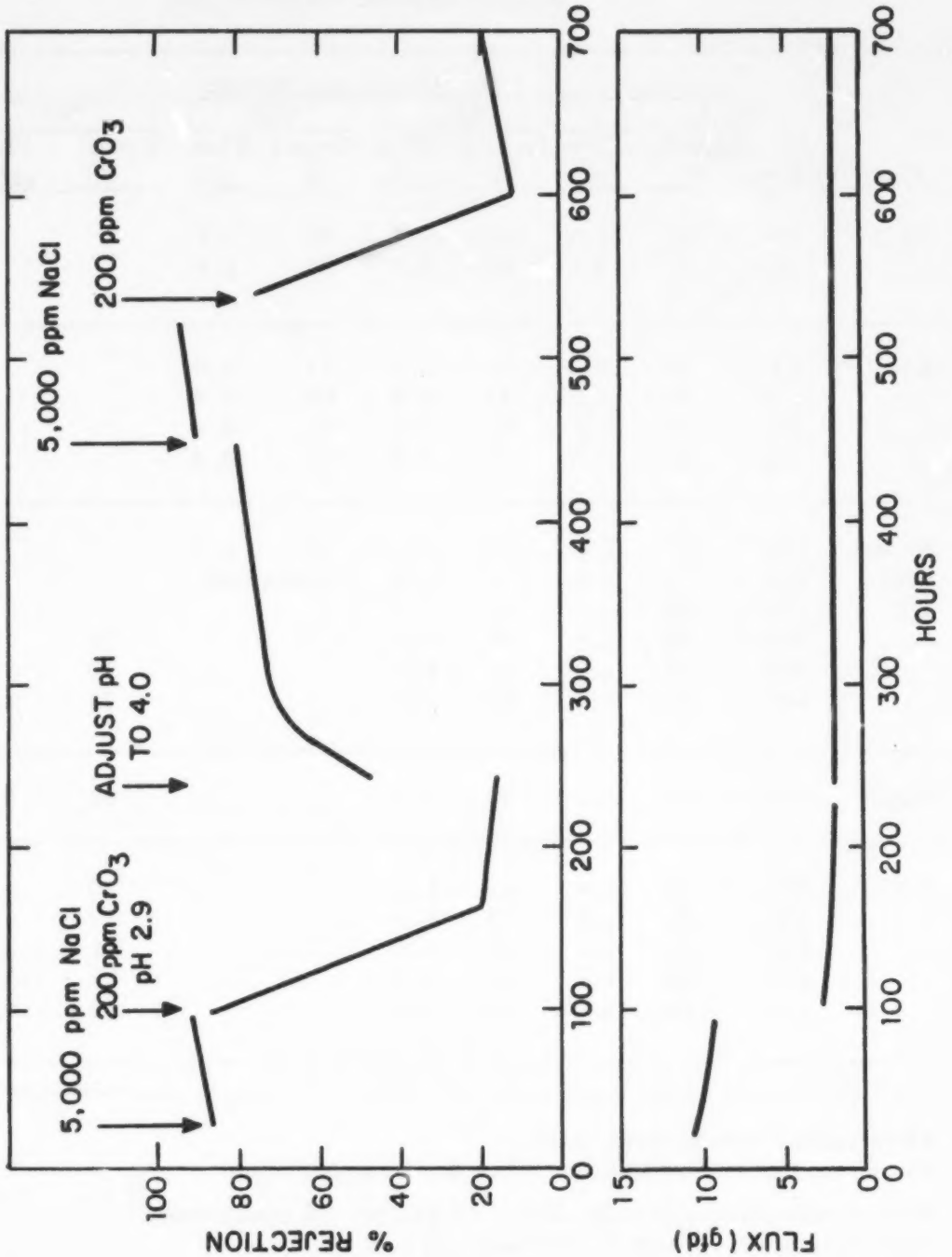


TABLE 5. RO PROPERTIES OF TUNGSTATE-TREATED MEMBRANES

Feed	Test Hours	Membrane Sample 1 Reject. %	1 Flux gfd	2 Reject. %	2 Flux gfd	3 Reject %	3 Flux gfd
Na_2WO_4	24	98	8.2	98	7.1	98	13
	48	98	7.3	99	6.5	98	12
CrO_3	48	-	-	-	-	-	-
	72	90	3.9	90	3.9	90	7.2
	96	60	1.7	77	1.6	60	2.6
	125	48	1.3	53	1.4	50	2.6
	194	44	1.3	51	1.3	46	2.8
	218	46	1.2	50	1.4	49	2.7
	242*	47	1.4	51	2.0	45	4.1
	266	45	1.1	55	1.4	42	2.9

Test Conditions: 600 psig, 25°C, 20 gal/hr, 0% Conversion.

Feed Solutions: Sodium tungstate, Na_2WO_4; 5,000 ppm, pH 7.3.
Chromic acid, CrO_3; 200 ppm, pH 2.8-3.0.

*Raised pressure to 750 psig for 6 hours.

significantly better than the 22%-25% rejections for the same membranes at the end of the chromic acid test cycle reported in Table 4. Product fluxes for the three membranes in Table 5 ranged from 1.2 to 2.9 gfd. It is worth noting that during the conditioning period with 5,000 ppm sodium tungstate (pH 7.3), rejections as high as 98%-99% were obtained along with product flux ranging from 6.5 to 12 gfd. These results again show that the intrinsic RO properties of PBI membranes are not affected by long-term exposure to chromic acid rinse water.

Molybdate, another large oxygenated anion, was investigated as a conditioning agent for PBI membranes. Following the procedure used in the tungstate treatment, membranes were conditioned for 48 hours in the high pressure (600 psi) test loop with 5,000 ppm sodium molybdate solution, after which they were tested with 200 ppm chromic acid feed plus 2 ppm sulfuric acid. The results are reported in Table 6.

After 234 total test hours - - the last 186 hours or nearly eight days against chromic acid - - chromic acid rejections for the four membranes levelled off at about 30%. This is a significantly lower level of rejection than was achieved with the tungstate-treated membranes. Product flux values were similar, ranging from 1.4 gfd to 2.3 gfd. Again, as was observed in the tungstate treatment, very high solute rejections, ranging from 90% to 98%, were obtained in the conditioning period after 48 hours.

In order to obtain test data which more closely reflect actual plating operation conditions, an authentic chromium plating bath solution (33 oz/gal) was obtained and diluted down to a rinse water concentration of 200 ppm CrO_3. All subsequent membrane test results to be discussed below were obtained with the diluted plating solution. New membranes were prepared from the parent batch of 18% polymer solution.

The tungstate treatment was repeated and the treated membranes were tested against the diluted plating bath solution. Test results are given in Table 7 and very closely approximate those in Table 6 obtained with the simulated rinse water. Chromic acid rejection values for the four samples levelled off and after 8 days ranged from 42% to 60%. Product flux ranged from 1.3 to 2.1 gfd.

A modification of the tungstate treatment was investigated in an effort to obtain higher chromic acid rejection. This consisted of coagulating the freshly cast film in a 5% aqueous solution of sodium tungstate, instead of water alone, to entrain tungstate in the film. Annealing was then carried out in the manner previously described. On testing these membranes with dilute plating bath solution, the chromic acid rejection values were slightly lower than those obtained with the tungstate treated membranes in Tables 5 and 7. Test results are given in Table 8. The RO properties are

TABLE 6. RO PROPERTIES OF MOLYBDATE-TREATED MEMBRANES

Feed	Test Hours	Membrane Sample C-1 Reject. %	C-1 Flux gfd	C-2 Reject. %	C-2 Flux gfd	C-3 Reject. %	C-3 Flux gfd	C-4 Reject. %	C-4 Flux gfd
Na_2MoO_4	24	81	10.0	98	10.3	96	8.9	98	8.2
	48	90	6.6	98	9.2	96	7.6	98	8.1
CrO_3	48	-	-	-	-	-	-	-	-
	72	32	2.9	68	1.6	72	1.4	84	1.1
	96	23	2.7	57	1.6	52	1.4	67	1.2
	120	31	1.8	50	1.5	48	1.4	59	1.4
	144	32	1.8	53	1.5	47	1.3	60	1.1
	168	24	2.3	22	2.4	24	2.0	22	1.9
	234	27	2.3	34	1.9	34	1.6	34	1.4

Test Conditions: 600 psig, 25°C, 20 gal/hr, 0% Conversion

Feed Solutions: Sodium molybdate, Na_2MoO_4, 5,000 ppm, pH 7.6
Chromic acid, CrO_3 200 ppm + 2 ppm sulfuric acid, pH 2.9.

TABLE 7. RO PROPERTIES OF TUNGSTATE-TREATED MEMBRANES

Feed	Test Hours	Membrane Sample A-1 Reject %	A-1 Flux gfd	A-2 Reject. %	A-2 Flux gfd	A-3 Reject. %	A-3 Flux gfd	A-4 Reject. %	A-4 Flux gfd
Na_2WO_4	24	98	6.8	99	5.6	97	5.1	99	6.8
	48	98	5.4	99	4.2	98	4.2	99	5.6
CrO_3	48	-	-	-	-	-	-	-	-
	72	69	2.1	87	1.4	74	1.7	66	1.8
	96	49	1.9	71	1.3	53	1.5	48	1.7
	168	45	1.1	62	1.2	47	1.6	47	1.8
	238	42	2.1	60	1.3	43	1.6	43	1.9

Test Conditions: 600 psig, 25°C, 20 gal/hr, 0% Conversion

Feed Solutions: Sodium tungstate, Na_2WO_4; 5,000 ppm; pH 6.8.
Diluted plating bath solution, 175 ppm CrO_3, pH 3.0

TABLE 8. RO PROPERTIES OF MEMBRANES COAGULATED IN TUNGSTATE SOLUTION

Feed	Test Hours	Membrane Sample E-1 Reject. %	E-1 Flux gfd	E-3 Reject. %	E-3 Flux gfd	E-4 Reject. %	E-4 Flu gfd	E-5 Reject. %	E-5 Flux gfd
CrO_3	24	32	3.2	40	3.2	35	3.2	41	2.5
	48	34	3.4	43	3.5	39	3.3	39	2.8
	72	34	3.0	42	2.9	40	2.7	41	2.4

Test Conditions: 600 psig, 25°C, 20 gal/hr, 0% Conversion.

Feed Solutions: Sodium tungstate, Na_2WO_4; 5,000 ppm; pH 6.8.
Diluted plating bath solution, 175 ppm CrO_3, pH 3.0

significantly better, however, than those of untreated membranes, attesting to the beneficial effect of the tungstate anion on PBI membrane properties.

In yet another modification of the tungstate treatment and in a continued effort to achieve higher chromic acid rejections, 100 ppm sodium tungstate was added to the chromic acid feed solution. The membranes were first pretreated in the test loop with 5,000 ppm sodium tungstate feed solution as before. Percent rejection and flux values which were obtained in long-term testing are found in Table 9. These results clearly show that membrane performance improved significantly as a result of adding 100 ppm sodium tungstate to the feed. At 210 total test hours, 168 hours with the 200 ppm chromic acid plating solution, chromic acid rejection values had levelled off at 69%-74% for the four samples. The average value of 71% represents a significant improvement over the approximately 50% rejection value from tungstate pretreatment alone (Tables 5 and 7). Product flux values at 210 total test hours ranged from 2.0 to 2.9 gfd. These fluxes are higher than those obtained in Tables 5 and 7 for the pretreatment alone. Thus, the addition of tungstate anion to the feed raised the chromic acid rejection level to a useful, sustained level of 70% or more over 7 days, at which point the feed pH was raised to assess the effect of pH adjustment.

Highest rejections of hexavalent chromium were obtained when the pH of the feed, containing 200 ppm chromic acid, 100 ppm sodium tungstate and about 10 ppm sulfuric acid, was raised to pH 5.7 by addition of aqueous ammonia. At 48 hours after pH adjustment, rejections of chromium (+6) had risen to 95% and product flux increased substantially, ranging from 4.1 gfd to 6.0 gfd, as seen in Table 9.

Other membrane treatments were investigated but these proved ineffective in improving chromic acid rejection. One was the pretreatment with sodium fluosilicate and the other involved ionically crosslinking the polymer with perfluoroglutaric acid, a strong acid. Test results for the fluosilicate treatment are given in Table 10 and in Table 11 for the crosslinking case. It is seen that the chromic acid rejections for the fluosilicate-treated membranes were much lower than that achieved with the tungstate-treated membranes. Even lower rejections were observed with the crosslinked membranes.

The effects of the various membrane treatments and feed pH on chromic acid rejection are presented in Figure 3 for convenient comparison. Although membrane performance was improved by feed pH adjustment and membrane treatment, the project failed to develop a PBI membrane which would be acceptable in practice for the treatment of chromium plating rinse water.

TABLE 9. EFFECT OF TUNGSTATE ADDITION TO CHROMIC ACID FEED SOLUTION ON MEMBRANE RO PROPERTIES

Feed	Hours	Membrane Sample F-1 Reject. %	F-1 Flux gfd	F-2 Reject. %	F-2 Flux gfd	F-3 Reject. %	F-3 Flux gfd	F-4 Reject %	F-4 Flux gfd
Na_2WO_4	24	99.0	13.5	99.5	13.4	99.4	12.2	99.0	11.5
	48	99.4	11.2	-	11.0	99.4	9.7	98.9	9.3
CrO_3+ Na_2WO_4	48	-	-	-	-	-	-	-	-
	72	84	2.8	86	2.7	89	2.5	89	2.2
	96	78	3.0	81	2.9	85	2.1	85	2.2
	120	74	3.1	75	2.7	80	2.5	80	2.1
	168	74	2.9	77	2.8	79	2.4	79	2.1
	210	74	2.8	74	2.8	70	2.4	69	2.0
	234	91	6.7	91	6.1	90	5.3	94	4.7
	258	95	6.0	95	5.6	95	4.8	94	4.1

Test Conditions: 600 psig, 25°C, 20 gal/hr, O% Conversion

Feed Solutions: Sodium tungstate, 5,000 ppm, pH 7.2
Diluted plating bath solution, 200 ppm CrO_3+ 100 ppm sodium tungstate + 10 ppm sulfuric acid to bring to pH 3.0.

TABLE 10. RO PROPERTIES OF FLUOSILICATE TREATED MEMBRANES

Feed	Hours	Membrane Sample D-2 Reject. %	D-2 Flux gfd	D-3 Reject. %	D-3 Flux gfd	D-4 Reject. %	D-4 Flux. gfd	D-6 Reject. %	D-6 Flux gfd
Na_2SiF_6	24	82	1.7	85	1.8	71	2.1	59	1.6
	48	79	1.6	84	1.3	69	1.5	58	1.2
CrO_3	48	-	-	-	-	-	-	-	-
	72	55	1.1	41	1.6	31	2.3	31	2.6
	96	46	0.9	42	1.1	17	2.3	17	2.1
	120	39	1.0	38	1.2	19	2.2	10	2.5
	192	27	1.1	29	1.2	15	2.6	15	2.0

Test Conditions: 600 psig, 25°C, 20 gal/hr, 0% Conversion.

Feed Solutions: Sodium fluosilicate, Na_2SiF_6, 5,000 ppm, pH 3.8.
Chromic acid, CrO_3, 200 ppm, pH 3.0.

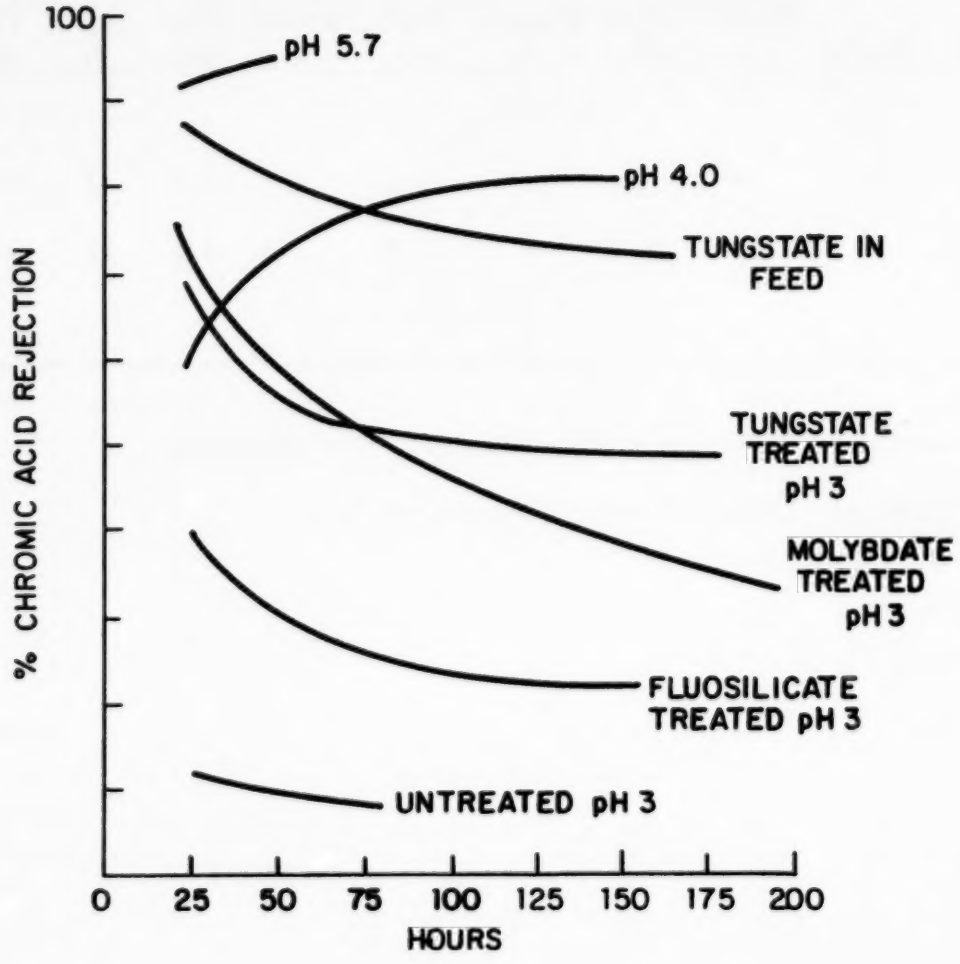
TABLE 11. RO PROPERTIES OF CROSSLINKED MEMBRANES

Feed	Hours	Membrane Sample G-1 Reject. %	G-1 Flux gfd	G-2 Reject. %	G-2 Flux gfd	G-3 Reject %	G-3 Flux gfd	G-4 Reject %	G-4 Flux gfd
CrO_3	24	10	12	10	7.2	12	5.9	14	5.0
	48	0	10.6	8	5.9	7.9	5.0	12	4.1

Test Conditions: 600 psig, 25°C, 20 gal/hr, 9% Conversion

Feed Solution: Chromic acid, 200 ppm, pH 3.0.

FIGURE 3: EFFECTS OF DIFFERENT MEMBRANE TREATMENTS AND FEED pH ON CHROMIC ACID REJECTION



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